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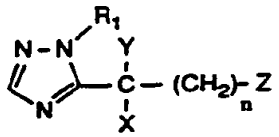
(54) Title: TRIAZOLE COMPOUNDS



(1)

(57) Abstract

This invention relates to a novel triazole compound represented by formula (1) wherein R_1 represents a hydrogen atom or a group A which is a protective group or is C_1-C_4-alkyl; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, a CH_2OH group, a $COOR_5$ group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; n is 0 or 1; and R_5 is a C_1-C_6-alkyl group, a process for preparing the same, a composition containing the same, as well as, application of the compound in the technical fields of herbicide or microbicides.

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DESCRIPTION

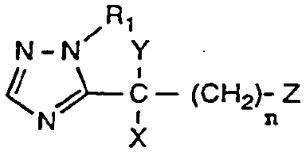
Triazole compounds

This invention relates to novel triazole compounds, processes for preparing the same, compositions containing the same, as well as, applications of the compounds in the technical fields of herbicides and microbicides.

Compounds of various chemical structures having herbicidal or microbicidal action have so far been developed to provide various and particularly selective herbicides and microbicides. Under such circumstances, more emphasis is being put on the protection of environment, and development of such herbicides and microbicides as do not cause environmental disruption neither secondarily nor later is desired.

Triazole compounds which have a herbicidal action are generally known. For example, European Patent Application No. 0 078 613 describes herbicidally active triazole compounds.

First of all, this invention relates to novel compounds represented by formula (1):

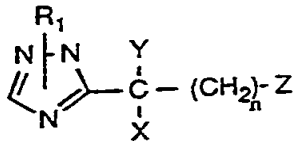


(1)

wherein R_1 represents a hydrogen atom or a group A which is a protective group or is C_1-C_4-alkyl; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, a CH_2OH group, a $COOR_5$ group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium,

trialkylsulfoxonium, phosphonium or amidinium cation;
n is 0 or 1; and
R_5 is a C_1-C_6-alkyl group.

This invention includes all of the isomers represented by the following formula of resonance structure:



(16)

in which R_1, n, X, Y and Z have the meanings as definded in formula (1).

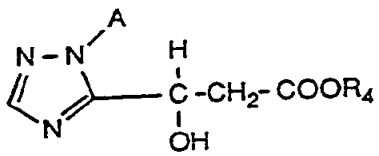
The present compound includes two kinds of compounds; one is phosphate compounds and the other phosphonate compounds.

Alkyl is, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and the various isomeric pentyl or hexyl radicals. The term "lower alkyl group" is preferably methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl or tert-butyl.

The meaning $-SiR'_3$ (wherein R' represents an alkyl group) also includes, for example, $-Si(CH_3)_3$, $Si(C_2H_5)_2CH_3$ or $Si(CH_3)_2$-$CH(CH_3)_3$.

The compounds represented by formula (1), wherein n is 1 and Z represents $-CH_2OPO(OR_3)_2$, can be prepared by:

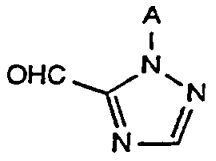
forming a ((1,2,4)-triazol-5-yl)propionic acid ester represented by formula (7):



(7)

wherein R_4 represents an alkyl group; and A has the same meaning as defined below,

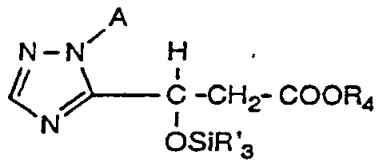
from a ((1,2,4)-triazol-5-yl)aldehyde represented by formula (6):



(6)

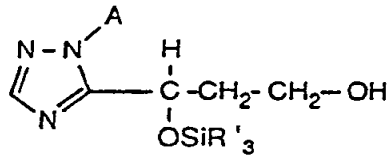
wherein A represents a protective group;

reacting the ((1,2,4)-triazol-5-yl)propionic acid ester thus formed with a suitable alkylsilyl halide to form a 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)propionic acid ester represented by formula (8):



(8)

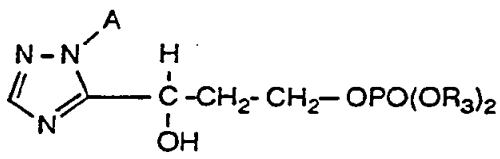
wherein R' represents an alkyl group; and A and R_4 have the same meanings as defined above, reducing the 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)-propionic acid ester to form a 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)-1-propanol represented by the formula (9):



(9)

wherein R' and A have the same meanings as defined above;

reacting the 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)-1-propanol with a suitable phosphine compound followed by desilylation to form a 3-hydroxy-3-((1,2,4)-triazol-5-yl)propyl-phosphate represented by formula (10):

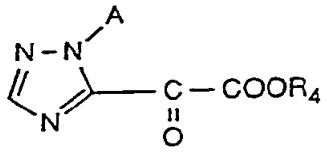


(10)

wherein R_3 and A have the same meaning as defined above; and converting, as necessary, the 3-hydroxy-3-((1,2,4)-triazol-5-yl)propyl-phosphate to 3-hydroxy-3-((1,2,4)-triazol-5-yl)propyl-phosphate (mono- or tri-ester form).

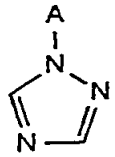
The compounds of the formula (1), wherein n is 0 and Z represents $-CH_2OPO(OR_3)_2$ can be prepared by:

forming a 2-((1,2,4)-triazol-5-yl)-2-oxoacetic acid ester represented by formula (11):



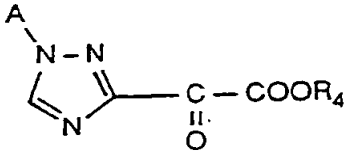
(11)

wherein R_4 represents an alkyl group; and A has the same meaning as defined below, from a (1,2,4)-triazole represented by formula (12):



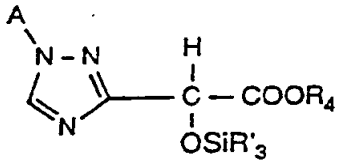
(12)

wherein A represents a group which is a protective group or is C_1-C_4-alkyl; isomerizing the 2-((1,2,4)-triazol-5-yl)-2-oxoacetic acid ester thus formed to form 2-((1,2,4)-triazol-3-yl)-2-oxoacetic acid ester represented by formula (13):



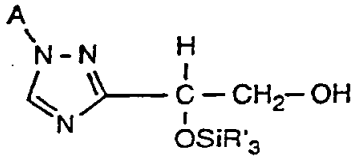
(13)

wherein A and R_4 have the same meanings as defined above; reducing the 2-((1,2,4)-triazol-3-yl)-2-oxoacetic acid ester followed by silylation to form 2-((1,2,4)-triazol-3-yl)-2-alkylsilyloxy-acetic acid ester represented by formula (14):



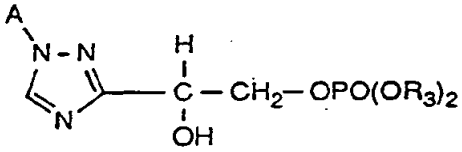
(14)

wherein R' represents an alkyl group; and A and R_4 have the same meanings as defined above, reducing the 2-alkylsilyloxy-2-((1,2,4)-triazol-3-yl)acetic acid ester to form a 2-alkylsilyloxy-2-((1,2,4)-triazol-3-yl)-1-ethanol represented by formula (15):



(15)

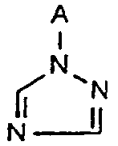
wherein R' and A have the same meanings as defined above; reacting the 2-alkylsilyloxy-2-((1,2,4)-triazol-3-yl)-1-ethanol with a suitable phosphine compound followed by desilylation to form a 2-hydroxy-2-((1,2,4)-triazol-3-yl)ethyl-phosphate represented by formula (16):



(16)

wherein A and R_3 have the same meaning as defined above; and converting, as necessary, the 2-hydroxy-2-((1,2,4)-triazol-3-yl)ethyl-phosphate to 2-hydroxy-2-((1,2,4)-triazol-3-yl)-ethyl-phosphate (mono or triester form); whereas the compounds of formula (1), wherein n is 1 and Z represents $-CH_2PO(OR_3)_2$ can be prepared by

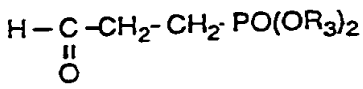
reacting a (1,2,4)-triazole represented by formula (12):



(12)

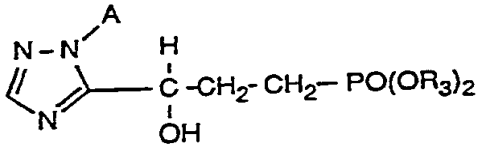
wherein A represents a group which is a protective group or is C_1-C_4-alkyl; with an

aldehyde compound represented by the formula (23):



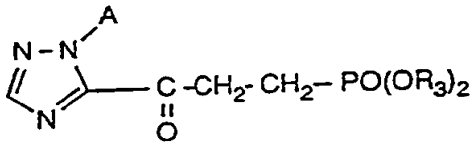
(23)

wherein R_3 has the same meaning as defined above, to form a 3-((1,2,4)-triazol-5-yl)-3-hydroxypropyl-phosphonate represented by formula (24):



(24)

wherein R_3 and A have the same meanings as defined above; converting the 3-((1,2,4)-triazol-5-yl)-3-hydroxypropyl-phosphonate to 3-(1H-1,2,4-triazol-5-yl)-3-hydroxy-propyl-phosphonic acid or phosphonate or oxidizing said 3-((1,2,4)triazol-5-yl)-3-hydroxypropyl-phosphonate to form a 3-((1,2,4)-triazol-5-yl)-3-oxopropyl-phosphonate represented by formula (25)

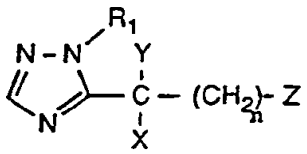


(25)

wherein R_3 and A have the same meanings as defined above, followed by conversion into 3-(1H-1,2,4-triazol-5-yl)-3-oxopropyl-phosphonic acid or phosphonate.

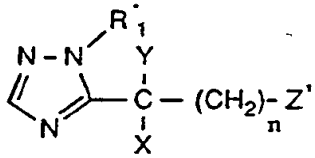
In the processes of this invention, A as a protective group may not be limited so long as it is conventionally used for inhibiting the reaction of triazole ring in synthetic organic chemistry and includes, for example, triphenylmethyl group, benzyl group, tert-butoxy-carbonyl group, allyl group and sulfonyl group.

Various intermediates formed in the above processes of forming the present compounds are novel compounds. Therefore the intermediate compounds represented by formulae (7), (8), (9), (10), (11), (13), (14), (15), (16), (24) and (25) are also included in this invention. Accordingly, the compounds of formula (1):



(1)

wherein R_1 represents a hydrogen atom or a group A which is a protective group or is C_1-C_4-alkyl; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, a CH_2OH group, a $COOR_5$ group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;
n is 0 or 1; and R_5 is a C_1-C_6-alkyl group, are all inclusive of the compounds of formula (2)



(2)

wherein R_1' represents a hydrogen atom or C_1-C_4-alkyl; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z' represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and
n is 0 or 1; and the above intermediate compounds, and therefore constitute the gist of this invention.

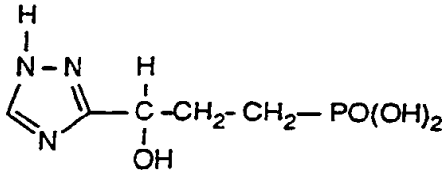
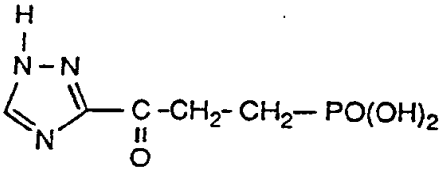
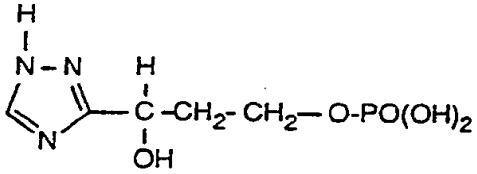
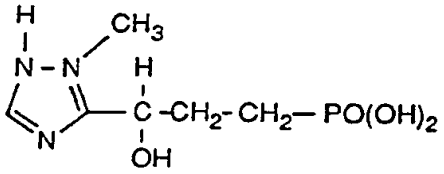
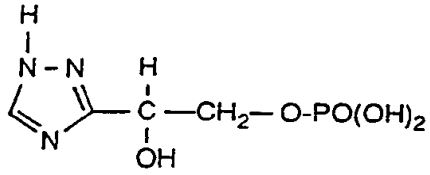
Preferred compounds of the formula (1) are those, in which
R_1 represents a hydrogen atom or a group A which is a protective group; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group or an allyl group or a CH_2OH group or a $COOR_5$ group,
n is 1; and
R_5 is an alkyl group, preferably a C_1-C_4-alkyl group.

Preferred compounds of the formula (2) are those, in which R_1' represents a hydrogen atom ; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z' represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and
n is 0 or 1, preferably 1.

Most especially prominent groups of compounds of formula (2) are those wherein X and Y independently represent a $-OR_2$ group, wherein R_2 represents an acetyl group.

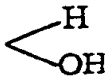
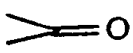
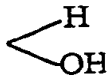
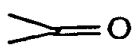
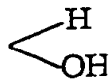
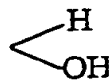
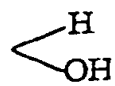
Particularly preferred of all the present compounds are described in table A:

Table A:

Compound No.	Structure
1	
2	
3	
102	
106	

Typical examples of these and other compounds according to this invention will be listed in the following Table 1; wherein Me represents a methyl group; Et represents an ethyl group; Bn represents a benzyl group, Acetyl represents an acetyl group; CPh_3 represents a triphenylmethyl group; Ph represents a phenyl group, Boc represents a 5-butoxycarbonyl group; and tBu represents a t-butyl group.

Table 1:

Comp. No.	R_1		Z' *	physical data
1	H		$P(O)(OH)_2$	m.p. 108°C
2	H		$P(O)(OH)_2$	m.p. 196-198°C
3	H		$OP(O)(OH)_2$	m.p. 40-43°C
4	H		$OP(O)(OH)_2$	
5	H		$P(O)(OEt)_2$	oil
6	H		$P(O)(OEt)_2$	
7	H		$OP(O)(OEt)_2$	
8	H		$OP(O)(OEt)_2$	
9	H		$P(O)(OBn)_2$	
10	H		$P(O)(OBn)_2$	

* $Z = -CH_2Z'$

Table 1 (Continuation)

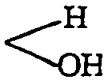
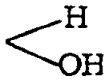
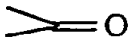
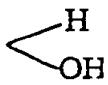
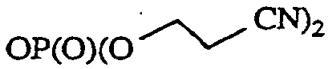
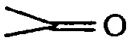
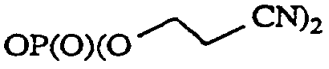
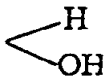
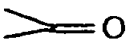
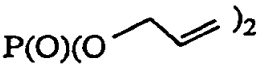
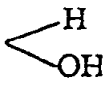
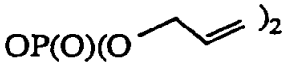
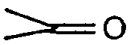
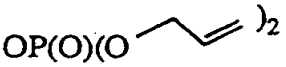
Comp. No.	R_1		Z'	physical data
11	H		$OP(O)(OBn)_2$	
12	H		$OP(O)(OBn)_2$	
13	H			
14	H			
15	H			
16	H			
17	H			
18	H			
19	H			
20	H			

Table 1 (Continuation)

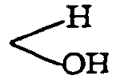
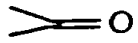
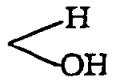
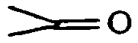
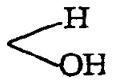
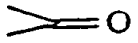
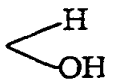
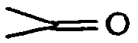
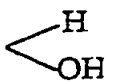
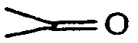
Comp. No.	R_1		Z'	physical data
21	CPh_3		$P(O)(OEt)_2$	m.p. 190-192°C
22	CPh_3		$P(O)(OEt)_2$	
23	CPh_3		$OP(O)(OEt)_2$	
24	CPh_3		$OP(O)(OEt)_2$	
25	CPh_3		$P(O)(OBn)_2$	
26	CPh_3		$P(O)(OBn)_2$	
27	CPh_3		$OP(O)(OBn)_2$	
28	CPh_3		$OP(O)(OBn)_2$	
29	CPh_3			
30	CPh_3			

Table 1 (Continuation)

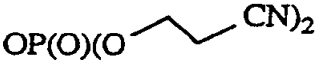
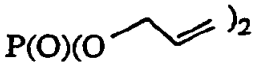
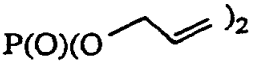
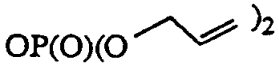
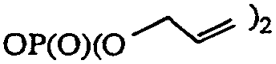
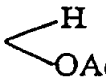
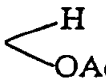
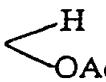
Comp. No.	R_1		Z'	physical data
31	CPh_3			
32	CPh_3			
33	CPh_3			
34	CPh_3			
35	CPh_3			
36	CPh_3			
37	CPh_3		$P(O)(OEt)_2$	m.p. 165-166°C
38	CPh_3		$OP(O)(OEt)_2$	
39	CPh_3		$P(O)(OBn)_2$	
40	CPh_3		$OP(O)(OBn)_2$	

Table 1 (Continuation)

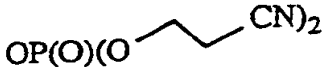
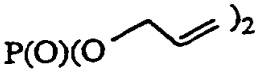
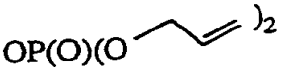
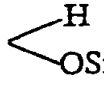
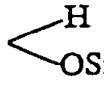
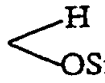
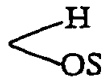
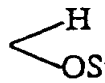
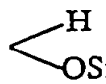
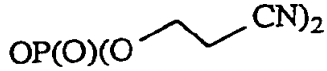
Comp. No.	R_1		Z'	physical data
41	CPh_3			
42	CPh_3			
43	CPh_3			
44	CPh_3			
45	CPh_3		$P(O)(OEt)_2$	
46	CPh_3		$OP(O)(OEt)_2$	
47	CPh_3		$P(O)(OBn)_2$	
48	CPh_3		$OP(O)(OBn)_2$	
49	CPh_3			
50	CPh_3			

Table 1 (Continuation)

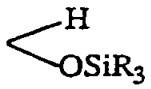
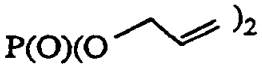
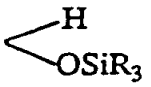
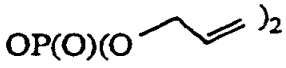
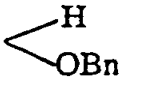
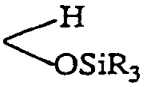
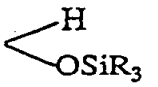
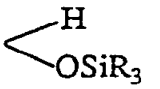
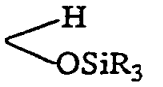
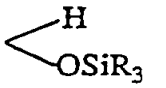
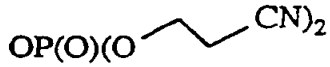
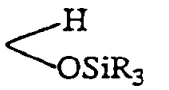
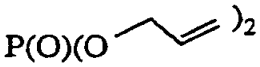
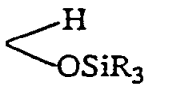
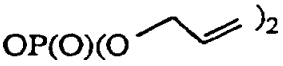
Comp. No.	R_1		Z'	physical data
51	CPh_3			
52	CPh_3			
53	CPh_3		$P(O)(OEt)_2$	
54	CPh_3		$OP(O)(OEt)_2$	
55	CPh_3		$P(O)(OBn)_2$	
56	CPh_3		$OP(O)(OBn)_2$	
57	CPh_3			
58	CPh_3			
59	CPh_3			
60	CPh_3			

Table 1 (Continuation)

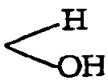
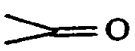
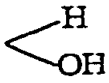
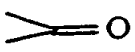
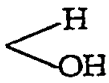
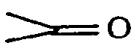
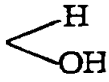
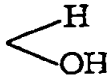
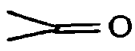
Comp. No.	R_1		Z'	physical data
61	Bn		$P(O)(OH)_2$	
62	Bn		$P(O)(OH)_2$	
63	Bn		$OP(O)(OH)_2$	
64	Bn		$OP(O)(OH)_2$	
65	Bn		$P(O)(OEt)_2$	
66	Bn		$P(O)(OEt)_2$	
67	Bn		$OP(O)(OEt)_2$	
68	Bn		$OP(O)(OEt)_2$	
69	Bn		$P(O)(OBn)_2$	
70	Bn		$P(O)(OBn)_2$	

Table 1 (Continuation)

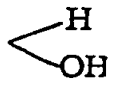
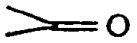
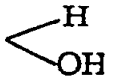
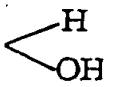
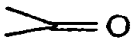
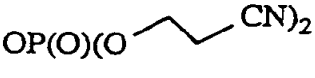
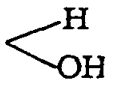
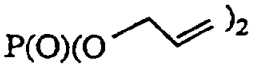
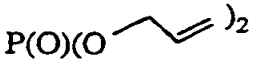
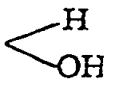
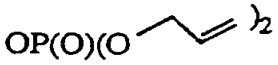
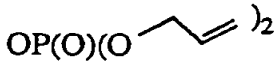
Comp. No.	R_1		Z'	physical data
71	Bn		$OP(O)(OBn)_2$	
72	Bn		$OP(O)(OBn)_2$	
73	Bn			
74	Bn			
75	Bn			
76				
77	Bn			
78	Bn			
79	Bn			
80	Bn			

Table 1 (Continuation)

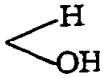
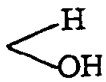
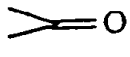
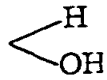
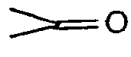
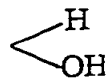
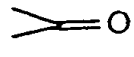
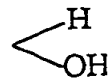
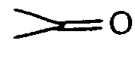
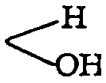
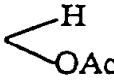
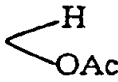
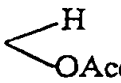
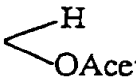
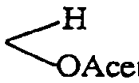
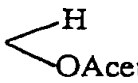
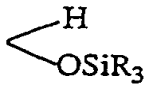
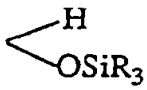
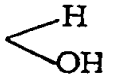
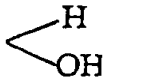
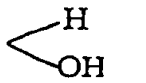
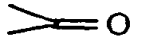
Comp. No.	R_1		Z'	physical data
81	CPh_3		$P(O)(OtBu)_2$	
82	CPh_3		$P(O)(OtBu)_2$	
83	CPh_3		$OP(O)(OtBu)_2$	
84	CPh_3		$OP(O)(OtBu)_2$	
85	Bn		$P(O)(OtBu)_2$	
86	Bn		$P(O)(OtBu)_2$	
87	Bn		$OP(O)(OtBu)_2$	
88	Bn		$OP(O)(OtBu)_2$	
89	Boc		$P(O)(OtBu)_2$	
90	Boc		$P(O)(OtBu)_2$	

Table 1 (Continuation

Comp. No.	R_1		Z'	physical data
91	Boc		$OP(O)(OtBu)_2$	
92	Boc		$OP(O)(OtBu)_2$	
93	CPh_3		$P(O)(OtBu)_2$	
94	Bn		$P(O)(OtBu)_2$	
95	Boc		$P(O)(OtBu)_2$	
96	CPh_3		$OP(O)(OtBu)_2$	
97	Bn		$OP(O)(OtBu)_2$	
98	Boc		$OP(O)(OtBu)_2$	
99	CPh_3		$OP(O)(OtBu)_2$	
100	Bn		$OP(O)(OtBu)_2$	
101	CH_3		$P(O)(OC_2H_5)_2$	oil
102	CH_3		$P(O)(OH)_2$	m.p. 64-78°C
103	C_2H_5		$P(O)(OH)_2$	m.p. 127-130°C
104	C_2H_5		$P(O)(OH)_2$	

Comp. No.	R_1		Z'	physical data
105	H		$P(O)(OH)_2$	m.p. 100°C
106	H		$OP(O)(OH)_2$	

The compounds of formula (1), in particular represented by formula (2), are distinguished by microbicidal and herbicidal properties which render them excellent for use in crops of useful plants, in particular in cereals, cotton, soya, rape, maize and rice.

The invention also relates to herbicidal and microbicidal compositions which comprise a novel active ingredient of formula (2), and methods for inhibition of plant growth.

The active ingredients of formula (2) are as a rule employed successfully at rates of application of 0.001 to 4 kg/ha, in particular 0.005 to 2 kg/ha. The doses required for the desired action can be determined by experiments. It depends on the nature of the action, the development stage of the crop plant and of the weed and on the application conditions (location, time, method) and can, as a result of these parameters, be varied within wide ranges.

The compounds of formula (2) are employed in unaltered form, as obtainable by the synthesis, or preferably together with the auxiliaries conventionally used in formulation technology, and they are therefore processed in a known manner to give, for example, emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules, and also encapsulations, for example in polymeric substances. The application methods, such as spraying, atomising, dusting, scattering or pouring, as well as the type of compositions are selected to suit the intended aims and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or combinations comprising the active substance of formula (2) and, if desired, one or more solid or liquid additives, are

prepared in a known manner, for example by intimately mixing and/or grinding the active substances with extenders, for example with solvents, solid carriers and, if desired, surface-active compounds (surfactants).

The following are possible as solvents: aromatic hydrocarbons, in particular the fractions C_8 to C_{12}, such as mixtures of alkylbenzenes, for example xylene mixtures or alkylated naphthalenes; aliphatic and cycloaliphatic hydrocarbons such as paraffins, cyclohexane or tetrahydronaphthalene; alcohols, such as ethanol, propanol or butanol; glycols as well as their ethers and esters, such as propylene glycol or dipropylene glycol ether, ketones such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or water; vegetable oils as well as their esters, such as rapeseed oil, castor oil or soybean oil; and if appropriate also silicone oils.

Suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties, depending on the nature of the active substance of formula (2) to be formulated. Surfactants are also to be understood as meaning mixtures of surfactants.

Anionic surfactants which are suitable can be either so-called water-soluble soaps or water-soluble synthetic surface-active compounds.
Suitable soaps which may be mentioned are the alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts of higher fatty acids (C_{10}-C_{22}), such as the Na salts or K salts of oleic or stearic acid, or of natural mixtures of fatty acids which can be obtained, for example, from coconut oil or tallow oil. Mention must also be made of the fatty acid methyltaurinates.

However, so-called synthetic surfactants are used more frequently, in particular fatty alcohol sulfonates, fatty alcohol sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or fatty alcohol sulfates are generally in the form of alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts, and have an alkyl radical having 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals, for example the Na or Ca salt of ligninsulfonic acid, of the dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide

adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl groups and one fatty acid radical having 8 to 22 C atoms. Examples of alkylarylsulfonates are the Na, Ca or triethanolamine salts of dodecylbenzenesulfonic acid, of dibutylnaphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensation product.

Other suitable compounds are the corresponding phosphates, such as the salts of the phosphoric ester of a p-nonylphenol/(4-14)-ethylene oxide adduct, or phospholipids.

Suitable non-ionic surfactants are mainly polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, of saturated or unsaturated fatty acids and of alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols.

Other non-ionic surfactants which are suitable are the water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol which have 1 to 10 carbon atoms in the alkyl chain and which contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. The abovementioned compounds customarily contain 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of non-ionic surfactants which may be mentioned are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol.

Other suitable substances are fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylenesorbitan trioleate.

The cationic surfactants are mainly quaternary ammonium salts, which contain at least one alkyl radical having 8 to 22 C atoms as N-substituents and which have lower halogenated or free alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methylsulfates or ethylsulfates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants customary in formulation technology are described, inter alia, in the

following publications:
"McCutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, New Jersey, 1988;
M. and J. Ash. "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-1981.
Dr. Helmut Stache, "Tensid-Taschenbuch [Surfactant Guide]", Carl Hanser Verlag, Munich, Vienna, 1981;

As a rule, the pesticidal preparations contain 0.1 to 99 %, in particular 0.1 to 95 %, of the active substance of formula (2), 1 to 99 % of a solid or liquid additive and 0 to 25 %, in particular 0.1 to 25 %, of a surfactant.

While concentrated compositions are more preferred as commercial goods, the user generally uses dilute compositions.

The compositions can also comprise further additives such as stabilisers, for example epoxidised or unepoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), defoamers, for example silicone oil, preservatives, viscosity regulators, binders, tackifiers, as well as fertilisers or other active substances for achieving specific effects.

In particular, preferred formulations have the following composition: (% = per cent by weight)

Emulsifiable concentrates:

Active ingredient:	1 to 90 %, preferably 5 to 20 %
Surface-active agent:	1 to 30 %, preferably 10 to 20 %
Liquid carrier:	50 to 94 %, preferably 70 to 85 %

Suspension concentrates:

Active ingredient:	5 to 75 %, preferably 10 to 50 %
Water:	94 to 24 %, preferably 88 to 30 %
Surface-active agent:	1 to 40 %, preferably 2 to 30 %

As a rule, the active substances of formula (2) are sucessfully employed at application

rates from 0.001 to 10 kg/ha, in particular 0.005 to 2 kg/ha. The dosage rate which is required for the desired action can be determined by tests. It depends on the nature of the action, the development stage of the crop plant and the weed, as well as on the application (location, time, method) and, due to these parameters, can vary within wide limits.

Controlled release of active substance

The dissolved active substance is applied to mineral granule carriers or polymerised granules (urea/formaldehyde) and allowed to dry. If desired, a coating can be applied (coated granules), which permits slow release of the active substance over a certain period.

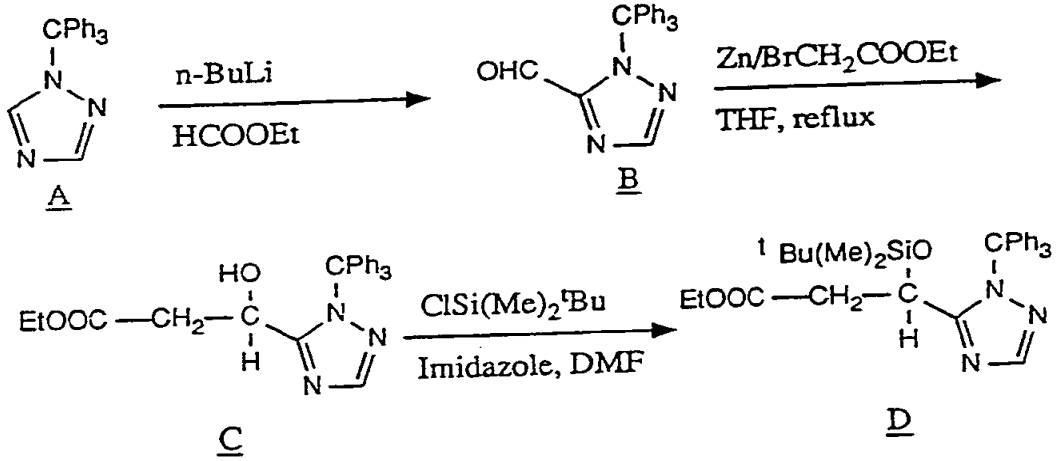
This invention further relates to the use of at least one of the compounds represented by formula (2) as the active ingredient for inhibiting enzymes which participate in the biosynthesis of histidine.

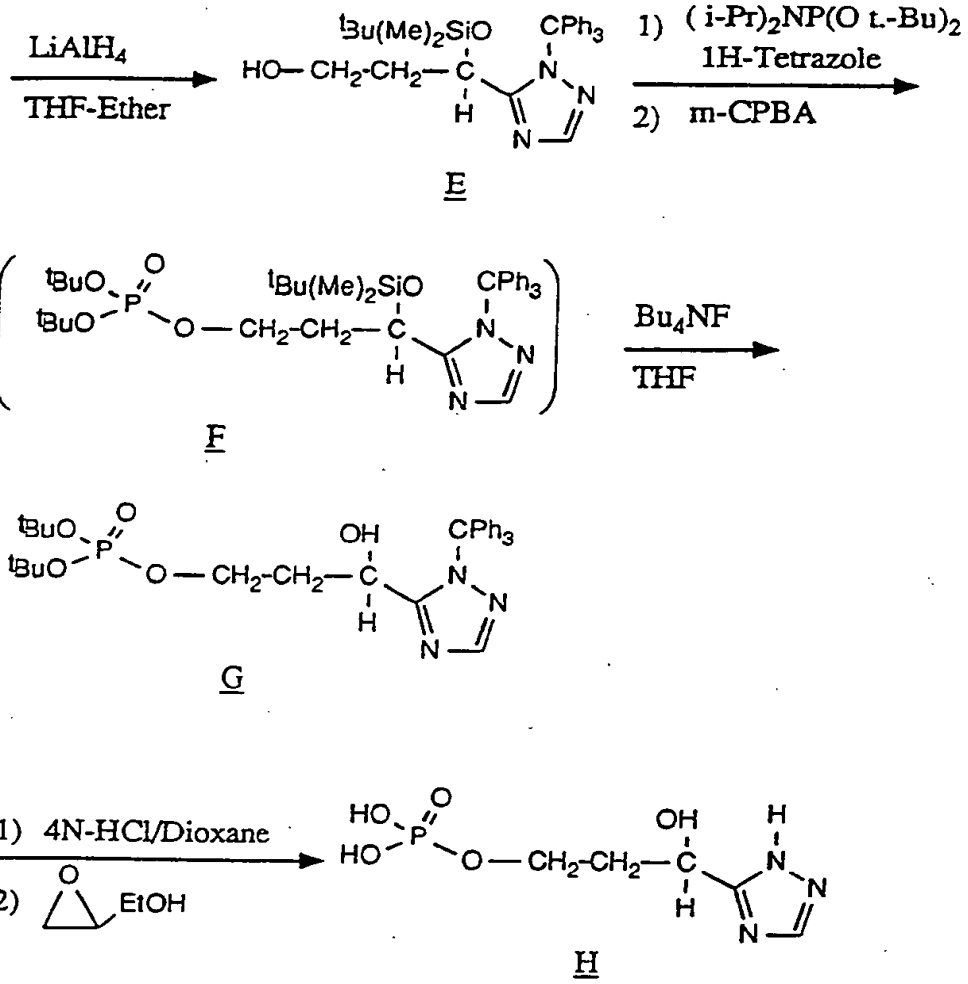
Example

This invention will be described below more specifically by way of Examples.

Example 1

A phosphate compound of this invention was prepared according to the flow charts shown below:





(1) ((1-Triphenylmethyl)-(1,2,4)-triazol-5-yl)aldehyde: Compound B

To a stirred solution of 1-triphenylmethyl-(1,2,4)-triazole (Compound A) (40 g, 0.129 mole) dissolved in 400 ml of THF was added n-BuLi (1.5 M hexane solution, 112 ml) at -78°C, and after the resulting mixture was stirred at the same temperature for 20 minutes, 17 g (0.23 mole) of ethyl formate was added thereto. After the resulting mixture was stirred for 10 minutes, the temperature of the reaction mixture was elevated to room temperature and then quenched to -78°C, followed by addition of a saturated aqueous NH_4Cl and extraction with $CHCl_3$. The $CHCl_3$ extract was collected, washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by recrystallization from ether to give 40 g of the desired compound B as a colorless powder (Yield 92 %).

^{1}H-NMR ($CDCl_3$, δ): 7.04-7.40 (15H, m) 8.09 (1H, s), 9.14 (1H, s)

IR ($CHCl_3$, cm^{-1}): 3075, 3025, 1720, 1708, 1600, 1495, 1450, 1430, 1335, 1325, 1285, 1220, 1100, 1075, 1040, 905, 890, 785, 760, 700, 670

(2) Ethyl 3-hydroxy-3-(1-triphenylmethyl-(1,2,4)-triazol-5-yl)-propionate: Compound C

To a stirred solution of Compound B (10 g, 29.5 mmoles) dissolved in 200 ml of THF were added successively 3.86 g (59 mmoles) of a zinc powder and 6.54 ml (59 mmoles) of ethyl acetate, and after the resulting mixture was refluxed for one hour, it was filtered through Celite. The filtrate was concentrated to give an oily residue, which was purified over silica gel column chromatography (hexane/ethyl acetate = 3:1 - 1:2) to obtain 5.84 g of Compound C as a substantially colorless oil (Yield 46.4 %).
^1H-NMR ($CDCl_3$, δ): 1.10 (3H, t J=7.0 Hz), 2.97 (2H, d J=7.9 Hz), 3.95 (2H, q, J=7.0 Hz), 4.22 (1H, brs), 6.35 (1H, t J=7.0 Hz), 6.8-7.5 (15H, m), 8.67 (1H, s)
IR (neat, cm^{-1}): 3430, 3150, 3070, 3000, 1730, 1600, 1530, 1490, 1470, 1450, 1400, 1375, 1330, 1270, 1220, 1190, 1165, 1090, 1065, 1040, 1005, 880, 760, 770

(3) Ethyl 3-tert-butyldimethylsilyloxy-3-(1-triphenylmethyl-(1,2,4)-triazol-5-yl)-propionate: Compound D

To a stirred solution of Compound C (12 g, 28.1 mmoles) dissolved in 100 ml of DMF were added successively 6.34 g (42 mmoles) of tert-butyldimethylsilyl chloride and 3.82 g (56.2 mmoles) of imidazole, and after the mixture was stirred at room temperature for 3 hours, the reaction mixture was quenched with ice water, extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified over silica gel column chromatography (hexane/ethyl acetate = 4:1) to obtain 14.17 g of Compound D as a colorless oil (Yield 93.2 %).
^1H-NMR ($CDCl_3$, δ): 0.00 (3H, s), 0.13 (3H, s), 0.92 (9H, s), 1.33 (3H, t, J=7.3 Hz), 3.0 (2H, m), 4.17 (2H, q J=7.3 Hz), 5.45 (1H, dd, J=5.5 Hz, J=8 Hz), 7.2-7.47 (15H, m), 8.0 (1H, s)
IR (neat, cm^{-1}): 2950, 2930, 2855, 1735, 1595, 1490, 1470, 1445, 1370, 1250, 1170, 1100, 1030, 1000, 955, 880, 840, 780, 760, 700

(4) 3-tert-Butyldimethylsilyloxy-3-(1-triphenylmethyl-(1,2,4)-triazol-5-yl)propanol: Compound E

To a stirred solution of Compound D (4.8 g, 8.9 mmoles) dissolved in THF/ether (60 ml:

30 ml) was added 505 mg (13.3 mmoles) of $LiAlH_4$ at -10°C, and after the mixture was stirred for 1 hour, the reaction mixture was quenced with 1N-KOH solution and then filtered through Celite. The filtrate was concentrated to give an oily residue, which was purified over silica gel chromatography (hexane/ethyl acetate = 1:1) to obtain 2.92 g of the desired compound E as a colorless oil (Yield 66 %).

^{1}H-NMR ($CDCl_3$, δ): -0.13 (3H, s), 0.00 (3H, s), 0.92 (9H, s), 2.20 (2H, M), 2.70 (1H, brs), 3.88 (2H, m), 5.20 (1H, t J=6.3 Hz), 7.15-7.45 (15H, m), 8.0 (1H, s)
IR (neat, cm^{-1}): 3375, 3060, 3030, 2950, 2850, 2880, 1600, 1510, 1490, 1450, 1390, 1360, 1325, 1250, 1190, 1170, 1000, 1030, 985, 940, 905, 880, 840, 770, 700, 670, 640

(5) Di-tert-butyl 3-hydroxy-3-(1-triphenylmethyl-(1,2,4)-triazol-5-yl)propyl-phosphate: Compound G

To a stirred solution of Compound E (7 g, 14 mmoles) dissolved in THF/CH_3CN (40 ml : 40 ml) were successively added 11.7 g (42.2 mmoles) of bis(tert-butoxy)(diisopropyl-amino)phosphine and 2.95 g (42 mmoles) of 1H-tetrazole at room temperature, and after the mixture was stirred for 1 hour, the reaction mixture was cooled to -40°C. To the mixture was slowly added a solution of m-CPBA (7.26 g, 42 mmoles) dissolved in CH_2Cl_2 (50 ml), and the resulting mixture was stirred at the same temperature for 10 minutes. After the temperature of the reaction mixture was elevated to room temperature, it was extracted with CH_2Cl_2. The extract was collected, washed successively with a 5 % aqueous $NaHSO_3$ solution, a saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated to give an oily residue (Compound F), and then THF (100 ml) and TBAF (1M THF solution, 40 ml) were added thereto at 0 to 5°C.

After the resulting mixture was stirred at room temperature for 18 hours, the reaction mixture was extracted with $CHCl_3$. The extract was collected, washed with water and brine, dried over $MgSO_4$ and concentrated to give an oily residue.

The thus obtained product was purified over silica gel chromatography ($CHCl_3$/acetone = 4:1) to obtain 5 g of Compound G as a colorless oil (Yield 62 %).

^{1}H-NMR ($CDCl_3$, δ): 1.47 (18H, s), 2.23 (2H, m), 3.56 (1H, brs), 4.18 (2H, m), 5.05 (1H, dd J=5.0 Hz, J=8.0 Hz), 7.05-7.4 (15H, m), 7.91 (1H, s)
IR (neat, cm^{-1}): 3350, 3070, 3025, 2975, 2940, 2910, 2875, 1720, 1670, 1600, 1510, 1495,

1478, 1450, 1395, 1370, 1345, 1330, 1250, 1170, 1100, 1020, 920, 880, 830, 800, 750, 705, 670, 640

(6) 3-Hydroxy-3-(1H-(1,2,4)-triazol-5-yl)propyl-phosphate: Compound H

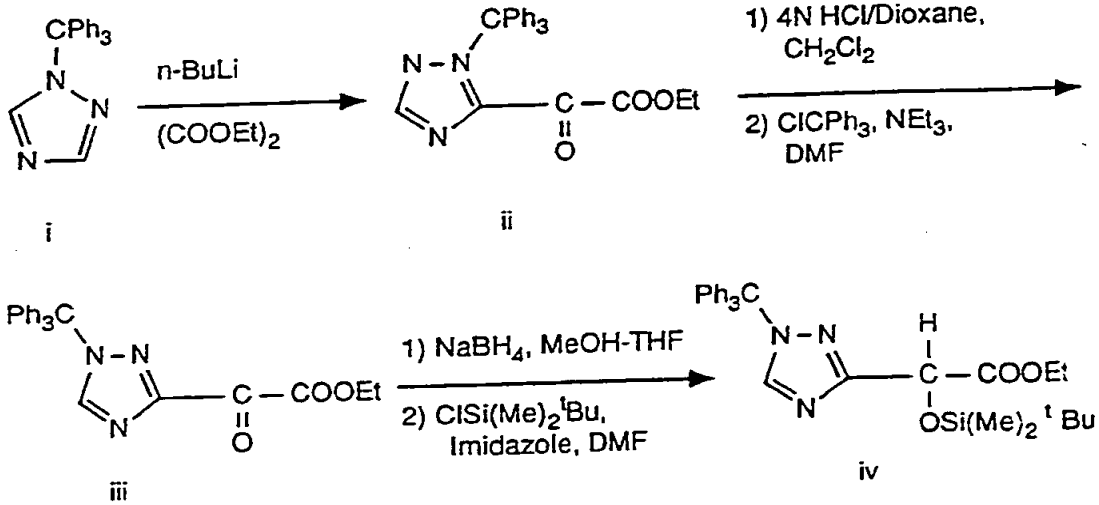
To a stirred solution of Compound G (1.0 g, 1.74 mmoles) dissolved in CH_2Cl_2 (5 ml) was added 8 ml of 4N-HCl-dioxane solution at 0 to 5°C, and the resulting mixture was stirred at room temperature for 1 hour. After the solvent was removed, the oily residue was diluted with 4 ml of EtOH, and then 3 ml of propylene oxide and ether were added thereto. Crystals thus precipitated was collected, washed with ether and acetone and dried in vacuo to give 290 mg of Compound H as a colorless powder (Yield 74.6 %).

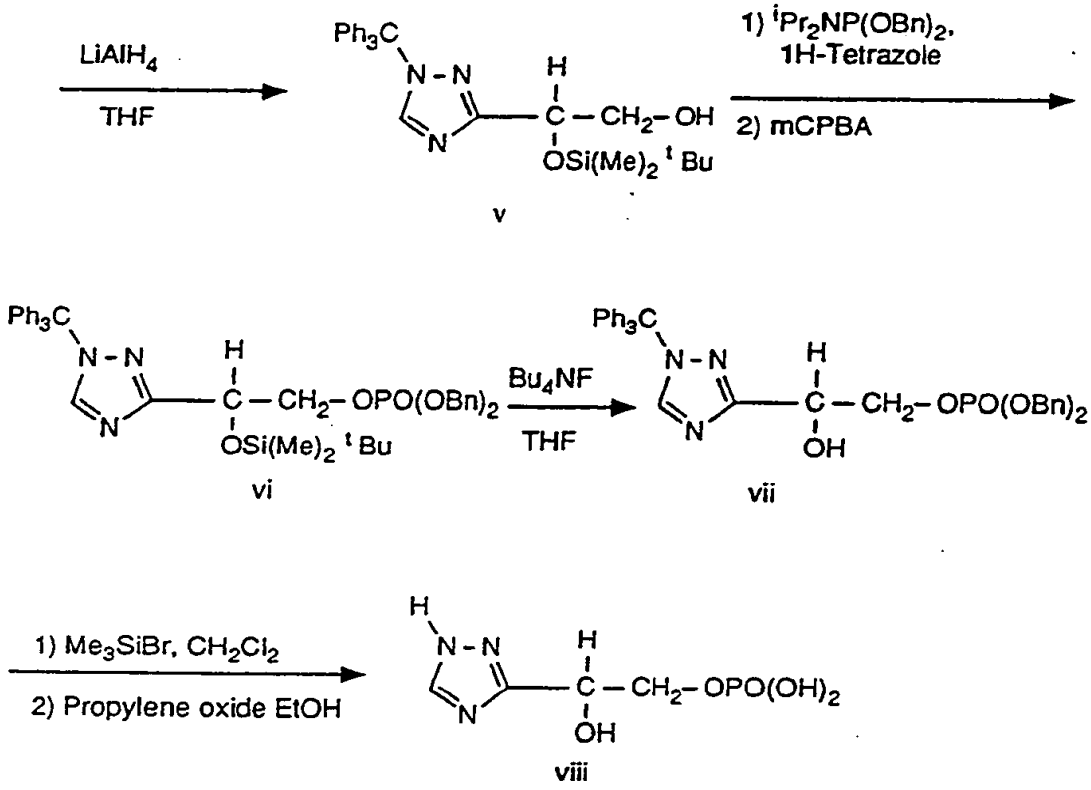
^{1}H-NMR (D_2O, δ): 2.25 (2H, m), 4.05 (2H,m), 5.30 (1H, t, J=6.0 Hz), 9.04 (1H, s)
m.p. 40 to 43°C

The thus obtained compound corresponds to the substance of Compound No. 3 in table 1.

Example 2

A phosphate compound of this invention was prepared according to the flow charts shown below:





(1) Ethyl 2-((1,2,4)-triazol-5-yl)-2-oxoacetate: Compound (ii)

To a stirred solution of 1-triphenylmethyl-(1,2,4)-triazole (compounds i) (50 g, 0.16 mol) dissolved in 750 ml of THF was added n-BuLi (1.5 M hexane solution, 0.24 mol) at -78°C. The resulting mixture was stirred for 30 min at the same temperature and 42 ml (0.31 mol) of diethyl oxalate was added thereto. After stirring for 10 min, the reaction mixture was warmed to room temperature and then quenched with saturated aqueous NH_4Cl, extracted with $CHVl_3$. The organic layer was collected, washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by recrystallization from ether to give 26 g of the compound (ii) as a colorless powder (Yield 39 %).

^{1}H-NMR ($CDCl_3$,δ): 8.07 (1H,s), 7.1-7.7 (15H,m) 4.27 (2H,q,J=7.0 Hz), 1.30 (3H,t, J=7.0 Hz)

(2) Ethyl 2-(1,2,4)-triazol-3-yl)-2-oxoacetate: Compound (iii)

To a stirred solution of compound (ii) dissolved in 150 ml of CH_2Cl_2 was added 35 ml

(140 mmol) of 4N HCl-dioxane at room temperature. After stirring for 30 min, the solvent was evaporated and the residue was dissolved in 50 ml of DMF. To this solution were added successively 1.8 g (6.5 mmol) of triphenylmethyl chloride and 23 ml (165.3 mmol) of triethylamine at 0-5°C. After the mixture was stirred to 1 h at room temperature, the reaction mixture was quenched with ice water extracted with ethyl acetate, washed with brine, dired over $MgSO_4$ and concentrated. The residue was purified by recrystallization from ether to give 18.8 g of the compound (iii) as a colorless powder (Yield 72,3 %).

^{1}H-NMR ($CDCl_3$, δ): 8.09 (1H,s), 7.0-7.6 (15H,m), 4.40 (2H,q,J=7.0 Hz), 1.30 (3H,t,J=7.0 Hz) IR (NaCl, cm^{-1}): 1750, 1710, 1690, 1490, 1465, 1440, 1255, 1170, 1090, 1050, 1035, 1010, 970, 870, 750, 700

(3) Ethyl 2-tert-butyldimethylsilyloxy-2-(1-triphenylmethyl-(1,2,4)-triazol-3-yl)-acetate: Compound (iv)

To a stirred suspension of $NaBH_4$ (556 mg, 14,87 mmol) in MeOH was added 5 g of compound (iii) (12.15 mmol) dissolved in MeOH-THF (15 ml-35 ml) at -40°C. After the mixture was stirred for 1 h, the reaction mixture was quenched with ice-water, extracted with $CHCl_3$, washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was dissolved in 60 ml of DMF and then 2.0 g (13.27 mmol) of tert-butyldimethylsilyl chloride and 1.2 g (17.64 mmol) of imidazole were successively added thereto at room temperature. After the mixture was stirred for 3 h, the reaction mixture was quenched with ice-water, extracted with $CHCl_3$, washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified over silica gel column chromatography ($CHCl_3$:acetone = 10:1) to give 4.36 g of the compound (iv) as colorless oil (Yield 74.2 %)

^{1}H-NMR ($CDCl_3$, δ): 7.91 (1H,s), 7.0-7.50 (15H,m), 5.43 (1H,s), 4.22 (2H,q,J=5.6 Hz), 1.25 (3H,t,J=5.6 Hz). 0.87 (9H,s), 0.10 (3H,s), 0.03 (3H,s)
IR (neat, cm^{-1}): 3060, 2955, 2925, 2900, 2860, 1760, 1738, 1595, 1490, 1470, 1460, 1445, 1370, 1360, 1340, 1330, 1250, 1130, 1030, 1000, 940, 880, 840, 780, 750, 700

(4) 2-tert-Butyldimethylsilyloxy-2-(1-triphenylmethyl-(1,2,4)-triazol-3-yl)ethanol: Compound (v)

To a stirred solution of compound (iv) (10 g, 18.95 mmol) dissolved in 200 ml of THF was added 270 mg (7.11 mmol) of $LiAlH_4$ at -15°C. After the mixture was stirred for 10 min, the reaction mixture was quenched with ice-water and then filtered through a

column of celite. The filtrate was concentrated to give oily residue which was purified over silica gel column chromatography (hexane:AcOEt = 2:1) to give 2.8 g of the compound (v) as a colorless powder (Yield 30.4 %).

^{1}H-NMR ($CDCl_3$, δ): 7.98 (1H,s), 7.0-7.6 (15H,m), 4.97 (1H,m), 3.95 (2H,m), 3.30 (1H,brs), 0.91 (9H,s), 0.09 (3H,s), 0.0 (3H,s)
IR (NaCl, cm^{-1}): 3350, 2925, 2850, 1600, 1505, 1490, 1470, 1460, 1445, 1355, 1250, 1170, 1100, 1060, 1040, 955, 870, 840, 780, 750, 700

(5) Dibenzyl 2-tert-butyldimethylsilyloxy-2-(triphenylmethyl-(1,2,4)-triazol-3-yl)ethyl phosphate: Compound (vi)

To a stirred solution of compouna (v) 2 g, 4.12 mmol) dissolved in 60 ml of CH_3CN were successively added 2.65 g (7.67 mmol) of bis(benzyloxy)-(diisopropylamino)phosphine and 869 mg (12.4 mmol) of 1H-tetrazole at room temperature and the mixture was stirred for 1 H. A solution of m-CPBA (1.53 g, 8.86 mmol) dissolved in 50 ml of CH_2Cl_2 wass added slowly at -78°C and the mixture was warmed to room temperature. The reaction was quenched with ice-water and extracted with CH_2Cl_2. The combined extracts were washed successively with 5 % aqueous $NaHSO_3$, saturated aqueous $NaHCO_3$, brine and dried over $MgSO_4$, concentrated in vacuo to afford oily residue which was purified over silica gel column chromatography (hexane:AcOEt = 1:1) to give 2.48 g of the compound (vi) as a colorless oil (Yield 80.6 %).

^{1}H-NMR ($CDCl_3$, δ): 7.97 (1H,s), 7.08-7.60 (25H,m), 4.91-5.19 (5H,m), 430 (2H,m), 0,89 (9H,s), 0,08 (6H,s)
IR (neat, cm^{-1}): 3060, 3040, 2950, 2925, 2880, 2855, 1517, 1492, 1475, 1380, 1350, 1310, 1285, 1215, 1070, 1060, 1130, 1085, 1010, 910, 878, 840, 780, 750, 700

(6) Dibenzyl-2-(hydroxy-2-(1-triphenylmethyl-(1,2,4)-triazol-3-yl)ethyl phosphae: Compound (vii)

To a stirred solution of compound (vi) (777 mg, 1.04 mmol) dissolved in 7 ml of THF was added 1.1 ml of Bu_4NF (1 M THF solution, 1.1 mmol). After the mixture was stirred at room temperature for 1 h, the reaction mixture was extracted with $CHCl_3$. The combined extracts were washed with water brine, dried over $MgSO_4$ and concentrated to give an oily residue which was purified over silica gel column chromatography (CH_2Cl_2:MeOH =

10:1) to give 215 mg of the compound (vii) as a colorless oil (Yield 32.7 %).

^{1}H-NMR ($CDCl_3$, δ): 7.90 (1H,s), 7.02-7.60 (25H,m), 5.05 (2H,s), 5.00 (1H,m), 4.96 (2Hs), 4.33 (3H,m)
IR (NaCl, cm^{-1}): 3350, 3075, 3025, 1495, 1445, 1270, 1215, 1175, 1090, 1020, 910, 880, 750, 700

(7) 2-Hydroxy-2-(1H-(1,2,4)-triazol-3-yl)ethyl phosphate: Compound (viii)

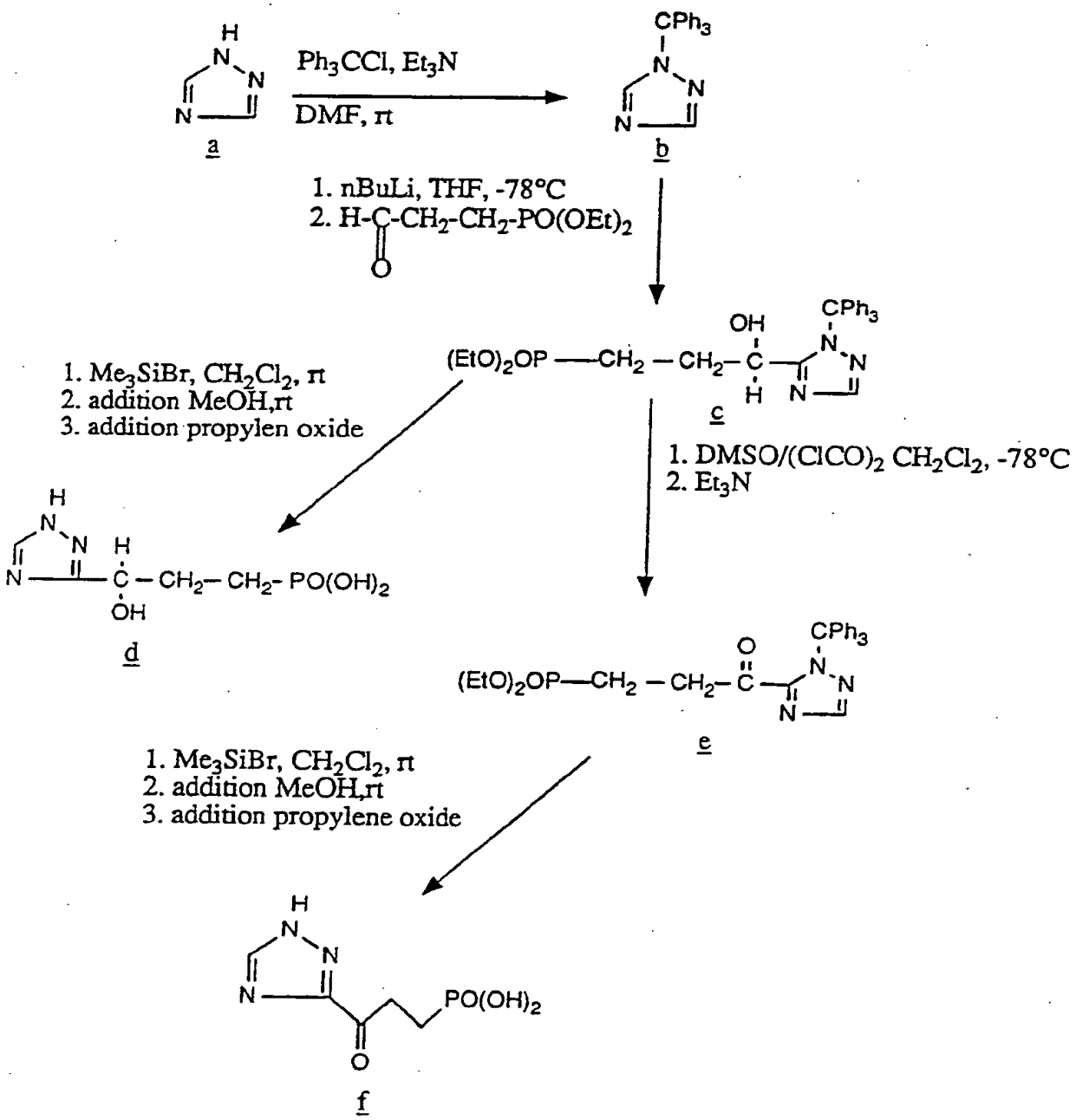
To a stirred solution of compound (vii) (310 mg, 0.49 mmol) dissolved in 3 ml of CH_2Cl_2 was added 0.26 ml (1.97 mmol) of Me_3SiBr at room temperature and the mixture was stirred for 1 h. Then 0.05 ml of EtOH was added and the mixture was stirred for another 1 h. To the solution were added propylene oxide (0.5 ml) and 5 ml of ether and the mixture was stirred at 0°C for 1 h. The gummy precipitates were collected, washed with ether and acetone, and dried in vacuo to give 50 mg of the compound (viii) (Yield 48.8 %).

^{1}H-NMR (D_2O, δ): 9.17 (1H,s), 5.25 (1H,t,J=4.0 Hz, 4.15 (2H,dd,J=7.0 Hz)

The thus obtained compound corresponds to the substance of compound No. 106 in table 1.

Example 3

A phosphonate compound of this invention was prepared according to the flow charts shown below:



(1) Diethyl 3-(1-triphenylmethyl-(1,2,4)-triazol-5-yl)-3-hydroxypropyl-phosphonate: Compound c

(1,2,4)-Triazole (Compound a) was protected with chlorotriphenylmethane to afford 1-triphenylmethyl-(1,2,4)-triazol (Compound b), and 4.67 g (15.0 mmoles) of the thus obtained Compound b was dissolved in 150 ml of THF. The resulting solution was cooled to -78°C and n-BuLi (1.5 M hexane solution, 16.5 mmoles) was added thereto dropwise

over 5 minutes. After the mixture was stirred at -78°C for one hour, 2.67 ml (15.0 mmoles) of an aldehyde prepared according to the process disclosed in DE 251634 was added thereto over 5 minutes, followed by stirring of the resulting mixture for 3 hours. The mixture was quenched to -78°C, and 5 ml of an aqueous NH_4Cl was added thereto. After the temperature of the mixture was elevated to room temperature, the mixture was diluted with 100 ml of ethyl acetate, washed successively with 200 ml of water and 50 ml of brine, dried over Na_2SO_4 and concentrated to give 5.72 g of a colorless solid. The solid was subjected to silica gel (175 g) chromatography using ethyl acetate and then CH_2Cl_2/CH_3OH = 19:1 to obtain 3.17 g of the title compound as a colorless solid (Yield 42 %).

m.p. 147 to 152°C

IR (NaCl) cm^{-1}: 3340, 1595, 1490, 1445, 1240, 1200, 1060, 1030, 960, 755, 700

^1H-NMR (90 MHz, $CDCl_3$) δ: 7.98 (1H, s), 7.05-7.53 (15H, m), 4.75 (1H, d, J=8.2 Hz), 4.02 (4H, quintet, J=7.4 Hz), 3.95-4.31 (1H, m), 1.50-2.10 (2H, m), 1.29 (6H, t, J=7.0 Hz), 0.55-1.15 (2H, m)

Elementary analysis for $C_{28}H_{32}O_4N_3P$

Calculated: C 66.52; H 6.38; N 8.31

Found C 66.57; H 6.46; N 8.02

(2) 3-(1H-1,2,4-triazol-3-yl)-3-hydroxypropyl-phosphonic acid: Compound d

To a solution of Compound c dissolved in 100 ml of CH_2Cl_2 was added 5.28 ml (40.0 mmoles) of Me_3SiBr, and the resulting mixture was stirred at room temperature overnight. To the mixture was added 25 ml of CH_3OH, and the resulting mixture was stirred at room temperature for one hour. Upon addition of 3.0 ml of propylene oxide, a gummy substance precipitated, which was dissolved by addition of CH_3OH (50 ml). When 400 ml of ether was slowly added to the solution, a micropowder precipitated. After stirring of the mixture at room temperature for one hour, the powder was filtered out, washed several times with ether and dried in vacuo to give 1.97 g of the title compound as a hygroscopic powder (Yield 95 %).

m.p. >60°C (decomp.)

^1H-NMR (90 MHz, D_2O) δ: 8.85 (1H, s), 5.11 (1H, t, J=6.3 Hz), 1.45-2.40 (4H, m)

The thus obtained compound corresponds to the substance of the Compound No. 1 in

Table 1.

(3) Compound e

To a solution of oxalyl chloride (0.69 ml, 7.91 mmoles) dissolved in 40 ml of methylene chloride was added dropwise 1.12 ml (15.8 mmoles) of dimethyl sulfoxide at -78°C over 10 minutes. After the resulting mixture was stirred for 15 minutes, a solution of Compound c (2.0 g, 3.69 mmoles) dissolved in 10 ml of methylene chloride was added thereto over 10 minutes, followed by stirring at -78°C for one hour. To the mixture was added 3.31 ml (23.8 mmoles) of triethylamine over 10 minutes, and the temperature of the mixture was elevated to room temperature over one hour. The reaction mixture was washed successively with 100 ml of water and brine, dried over Na_2SO_4 and concentrated to give 2.01 g of a colorless solid, which was subjected to silica gel chromatography using ethyl acetate to give 1.10 g of the title compound as a colorless solid (Yield 55 %).
m.p. 167 to 169°C
IR (NaCl) cm^{-1}: 2680, 1720, 1485, 1450, 1260, 1060, 1030, 960, 860, 801, 750, 700
^{1}H-NMR (90 MHz, $CDCl_3$) δ: 7.98 (1H, s), 6.91-7.40 (15H, m), 4.04 (4H, quintet, J=7.0 Hz), 2.87-3.14 (2H, m), 1.45-1.76 (2H, m), 1.28 (6H, t, J=7.0 Hz)

Elementary analysis for $C_{28}H_{30}O_4N_3P$
Calculated: C 66.78; H 6.01; N 8.35
Found C 66.64; H 6.07; N 8.21

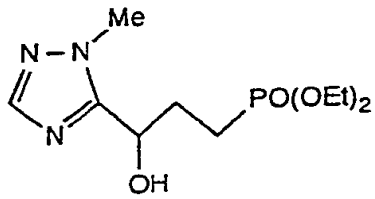
(4) 3-(1H-1,2,4-triazol-3-yl)-3-oxopropyl-phosphonic acid: Compound f

To a solution of Compound e (0.79 g, 1.57 mmoles) dissolved in 10 ml of methylene chloride was added 0.62 ml (4.71 mmoles) of trimethylsilyl bromide, and the resulting mixture was stirred at room temperature overnight. To the resulting mixture was added 6.0 ml of methanol, and the mixture was stirred for one hour. After addition of 2.0 ml of propylene oxid and stirring at room temperature for 15 minutes, 50 ml of ether was added to the mixture to effect crystallization of the desired product. The precipitate was collected, washed several times with ether and dried to give 0.34 g of the title compound as a white powder (Yield 100 %).
m.p. 196 to 198°C.
IR (NaCl) cm^{-1}: 1710, 1450, 1410
^{1}H-NMR (90 MHz, D_2O) δ: 8.66 (1H, s), 3.28-3.58 (2H, m), 1.98-2.35 (2H, m)

The thus obtained compound corresponds to the substance of the Compound No. 2 in Table 1.

Example 4:

Preparation of Diethyl 3-(1-Methyl-(1,2,4)-triazole-5-yl)-3-hydroxypropylphosphonate



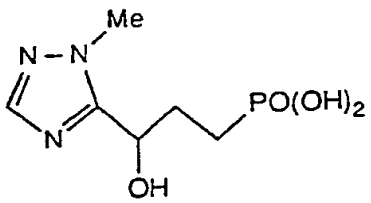
(Compound 101)

To a solution of 1-methyl-1,2,4-triazole (3.0 g, 36.1 mmol) in 60 ml of THF at -78°C under nitrogen was added n-BuLi (43.3 mmol, 1.5 M in hexane). After stirring for 1 h, diethyl-3-oxopropylphosphate (8.4 g, 43.3 mmol) was added and stirred for an additional 1 h. The reaction was quenched with aqueous saturated NH_4Cl (ca. 15 ml) and extracted with ethyl acetate (3 x 150 ml). The aqueous layer was saturated with NaCl and extracted further with dichloromethane (3 x 100 ml). The combined organic layers were dried over $MgSO_4$, concentrated, and purified by silica gel chromatography (AcOEt/EtOH) to give 3.60 g (30 % yield) of compound 101 as an oil.

^1H NMR (90 MHz, $CDCl_3$) δ; 7.78 (s, 1H), 5.00 (t, 1H,J=6.2 Hz), 4.20 (quint, 4,J=7.3), 4.00 (s,3H),2.50-1.60 (m,5H), 1.34 (t, 6H,J=7.0).

Example 5:

Preparation of (1-Methyl-(1,2,4)-triazole-5-yl)-3-hydroxypropylphosphonic acid



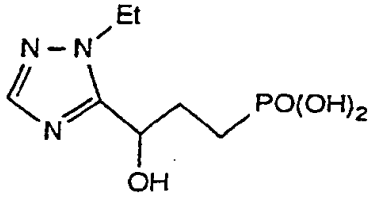
(Compound 102)

To a solution of compound 101 (2.0 g, 7.2 mmol) in 40 ml of dichloromethane was added

bromotrimethylsilane (4.74 mmol, 35.9 mmol) at room temperature under nitrogen and stirred for 17 h. After addition of 20 ml of methanol and stirring for 2 h, propylene oxide (2.0 ml) was added, stirred for 1 h, and diluted with ether. Precipitates were collected on a glass filter, washed with ether, and dried to give 1.0 g (63 % yield) of compound 102 as white powder. The melting point was obtained after lyophilizing from water.
mp; 64-74°C: ^{1}H-NMR (90 MHz, D_2O) δ; 8.39 (s, 1H), 5.23 (t, 1H,J=6.3), 4.02 (s,3H), 2.38-1.58 (m,4H).

Example 6:

Preparation of (1-Ethyl-(1,2,4)-triazol-5-yl)-3-hydroxypropylphosphonic acid



(Compound 103)

Compound 103 was prepared by the same procedure by starting with 1-ethyl-1,2,4-triazole instead of 1-methyl-1,2,4-triazole.

mp; 127-130°C: ^{1}H-NMR (90 MHz, D_2O) δ; 8.41 (s, 1H), 5.25 (t, 1H,J=6.5), 4.40 (q, 2H,J=7.4), 2.42-1.50 (m, 4H), 1.50 (t, 3H,J=7.4).

1-Methyl and 1-ethyl-1,2,4-triazole were prepared according to the procedure by Dallacker and Minn.

Dallacker, F.; Minn, K. Chemiker-Zeitung, 1986, 110, 101-108

Formulation examples of active substances of the formula (2)
(% = percent by weight)

1.Emulsion concentrates	a)	b)
Active substance from Table 1	10 %	1 %
Ca dodecylbenzenesulfonate	3 %	3 %
Octylphenol polyethylene glycol ether (4-5 mol of EO)	3 %	3 %

Castor oil polyethylene glycol ether (36 mol of EO)	4 %	4 %
Cyclohexanone	30 %	10 %
Xylene mixture	50 %	79 %

Emulsions of any desired concentration can be prepared from such concentrates by diluting them with water.

2.Suspension concentrate	a)	b)
Active substance from Table 1	5 %	40 %
Ethylene glycol	10 %	10 %
Nonylphenol polyethylene glycol ether (15 mol of EO)	1 %	6 %
Na ligninsulfonate	5 %	10 %
Carboxymethylcellulose	1 %	1 %
37 % aqueous formaldehyde solution	0.2 %	0.2 %
Silicone oil in the form of a 75% aqueous emulsion	0.8 %	0.8 %
Water	77 %	32%

The finely-ground active substance is mixed intimately with the additives. This gives a suspension concentrate, from which suspensions of any desired concentration can be prepared by diluting it with water.

3.Salt solution	
Active substance from Table 1	5 %
Isopropylamine	1 %
Octylphenol polyethylene glycol ether (78 mol of EO)	3 %
Water	91%

The compounds of the formula (2) are employed as such or preferably as compositions together with the auxiliaries customary in formulation technology, and they are therefore processed in a known manner to give, for example, emulsion concentrates, directly sprayable or dilutable solutions, dilute emulsions, sprayable powders, soluble powders, dusts, granules, and also encapsulations, for example in polymeric substances. The

application methods, such as spraying, atomising, dusting, scattering or pouring, as well as the type of compositions are selected to suit the intended aims and the prevailing circumstances.

Biological Examples

Example B1: Herbicidal action before emergence of the plants

The test plants are seeded out in plastic pots containing standard soil. Immediately after seeding, the pots are being sprayed with an aqueous suspension of the compound No. 102. The rate corresponds to 4000g a.i./ha. The treated pots are then placed in the greenhouse at temperatures of 18°C (night) and 24°C (day). Appr. 3 weeks after treatment, the emerged plants are evaluated in terms of herbicidal symtoms:

```
  1: plants have not emerged or are totally withered
2-3: very pronounced action
4-6: medium action
7-8: weak action
  9: no action (as untreated controls).
```

In this test, the compound 102 given in Table 1 shows very pronounced herbicidal action against the weeds.

Example B2: Post-emergence herbicidal action (contact herbicide)

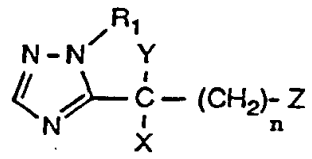
The test plants are seeded out in plastic pots containing standard soil and raised in the greenhouse at 18°C (night) and 24°C (day). Appr. 10 to 20 days after seeding (depending of individual growth-rate), foliar treatment takes place with an aqueous suspension of the compound No. 102. The rate corresponds to 2000g a.i./ha. Appr. 2 weeks after treatment, the emerged plants are evaluated in terms of herbicidal symtoms:

```
  1: plants have not emerged or are totally withered
2-3: very pronounced action
4-6: medium action
7-8: weak action
  9: no action (as untreated controls).
```

In this test, the compound 102 given in Table 1 shows very pronounced herbicidal action (rating "3") against the weed "Setaria" and medium action (rating "4") against the weed "Stellaria".

CLAIMS

1. A compound represented by formula (1)

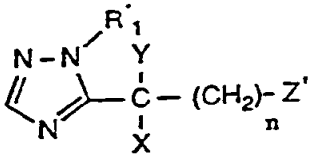


(1)

wherein R_1 represents a hydrogen atom or a group A which is a protective group or is C_1-C_4-alkyl; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, a CH_2OH group, a $COOR_5$ group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;
n is 0 or 1; and
R_5 is a C_1-C_6-alkyl group.

2. A compound of the formula (1) according to Claim 1, wherein
R_1 represents a hydrogen atom or a group A which is a protective group; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group or an allyl group or a CH_2OH group or a $COOR_5$ group,
n is 1; and
R_5 is a alkyl group.

3. A compound according to claim 1 of the formula (2)



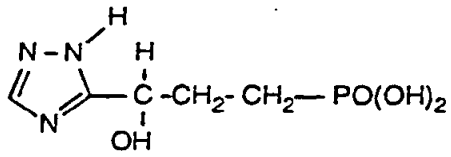
(2)

wherein R_1' represents a hydrogen atom or C_1-C_4-alkyl; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z' represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and
n is 0 or 1.

4. A compound according to claim 3, wherein
R_1' represents a hydrogen atom ; X and Y jointly represent a carbonyl group together with the carbon atom to which they are bonded, or X and Y each independently represent a hydrogen atom or a $-OR_2$ group, wherein R_2 represents a hydrogen atom, a lower alkyl group, an acetyl group, a benzyl group or a silyl group represented by $-SiR'_3$ (wherein R' represents an alkyl group); and Z represents a $-CH_2PO(OR_3)_2$ or $-CH_2OPO(OR_3)_2$ group (wherein R_3 represents a hydrogen atom, a lower alkyl group, a benzyl group, a phenyl group, a cyanoethyl group, an allyl group, or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and
n is 0 or 1.

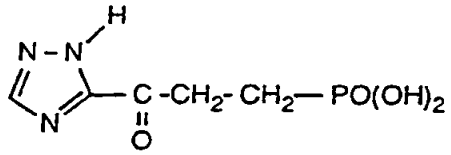
5. A compound according to Claim 3, wherein X and Y independently represent a $-OR_2$ group, wherein R_2 represents an acetyl group.

6. A compound according to Claim 3, wherein the compound is represented by formula (3):



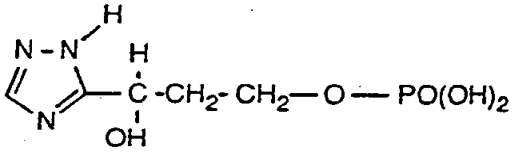
(3).

7. A compound according to Claim 3, wherein the compound is represented by formula (4):



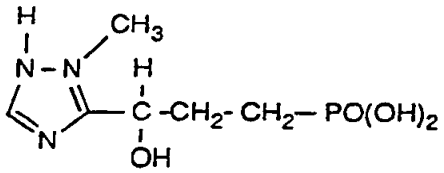
(4).

8. A compound according to Claim 3, wherein the compound is represented by formula (5):



(5).

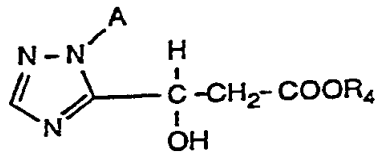
9. A compound according to Claim 3, wherein the compound is represented by formula (102):



(102).

10. A compound according to Claim 1, wherein the protective group A represents a triphenylmethyl group, a benzyl group, a tert-butoxycarbonyl group, an allylgroup or a sulfonyl group.

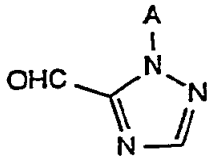
11. A process for producing the compound represented by formula (1) as claimed in Claim 1, wherein n is 1 and Z represents $-CH_2OPO(OR_3)_2$, which comprises: forming a ((1,2,4)-triazol-5-yl)propionic acid ester represented by formula (7):



(7)

wherein R_4 represents an alkyl group; and A has the same meaning as defined below,

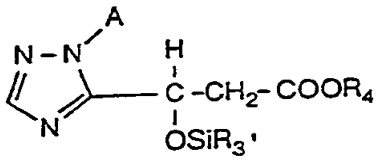
from a ((1,2,4)-triazol-5-yl)aldehyde represented by formula (6):



(6)

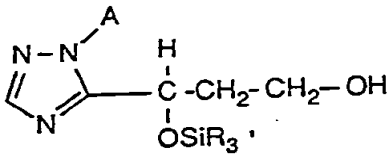
wherein A represents a protective group;

reacting the ((1,2,4)-triazol-5-yl)propionic acid ester thus formed with a suitable alkylsilyl halide to form a 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)propionic acid ester represented by formula (8):



(8)

wherein R' represents an alkyl group; and A and R_4 have the same meanings as defined above, reducing the 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)-propionic acid ester to form a 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)-1-propanol represented by the formula (9):

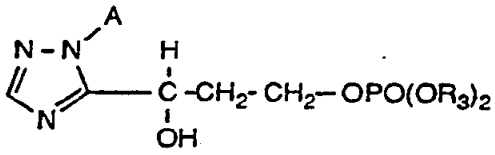


(9)

wherein R' and A have the same meanings as defined above;

reacting the 3-alkylsilyloxy-3-((1,2,4)-triazol-5-yl)-1-propanol with a suitable phosphine

compound to form a 3-hydroxy-3-((1,2,4)-triazol-5-yl)propyl-phosphate represented by formula (10):

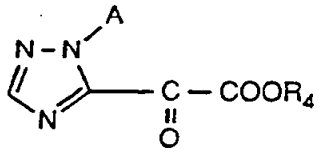


(10)

wherein R_3 has the same meaning as defined in Claim 1; and A has the same meaning as defined above; and converting, as necessary, the 3-hydroxy-3-((1,2,4)-triazol-5-yl)propyl-phosphate to 3-hydroxy-3-((1,2,4)-triazol-5-yl)propyl-phosphate (mono- or tri-ester form).

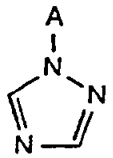
12. A process for producing the compound represented by the formula (1) as claimed in claim 1, wherein n is 0 and Z represents $-CH_2OPO(OR_3)_2$, which comprises:

forming a 2-((1,2,4)-triazol-5-yl)-2-oxoacetic acid ester represented by formula (11):



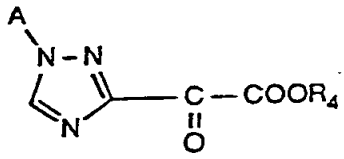
(11)

wherein R_4 represents an alkyl group; and A A represents a group which is a protective group or is C_1-C_4-alkyl, from a (1,2,4)-triazole represented by formula (12):



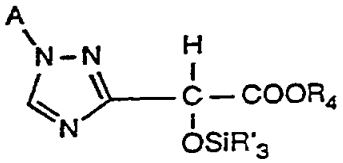
(12)

wherein A represents a group which is a protective group or is C_1-C_4-alkyl; isomerizing the 2-((1,2,4)-triazol-5-yl)-2-oxoacetic acid ester thus formed to form 2-((1,2,4)-triazol-3-yl)-2-oxoacetic acid ester represented by formula (13):



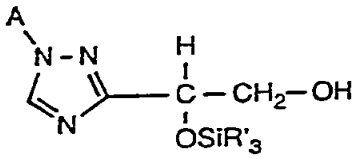
(13)

wherein A and R_4 have the same meanings as defined above; reducing the 2-((1,2,4)-triazol-3-yl)-2-oxoacetic acid ester followed by silylation to form 2-((1,2,4)-triazol-3-yl)-2-alkylsilyloxy-acetic acid ester represented by formula (14):



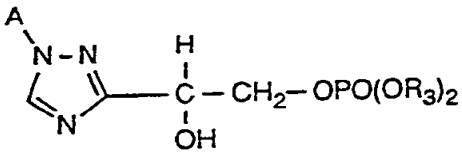
(14)

wherein R' represents an alkyl group; and A and R_4 have the same meanings as defined above, reducing the 2-alkylsilyloxy-2-((1,2,4)-triazol-3-yl)acetic acid ester to form a 2-alkylsilyloxy-2-((1,2,4)-triazol-3-yl)-1-ethanol represented by formula (15):



(15)

wherein R' and A have the same meanings as defined above; reacting the 2-alkylsilyloxy-2-((1,2,4)-triazol-3-yl)-1-ethanol with a suitable phosphine compound followed by desilylation to form a 2-hydroxy-2-((1,2,4)-triazol-3-yl)ethyl-phosphate represented by formula (16):



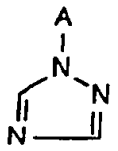
(16)

wherein A and R_3 have the same meaning as defined above; and converting, as necessary, the 2-hydroxy-2-((1,2,4)-triazol-3-yl)ethyl-phosphate to 2-hydroxy-2-((1,2,4)-triazol-3-yl)-ethyl-phosphate (mono or triester form).

13. A process for producing the compound represented by the formula (1) as claimed in

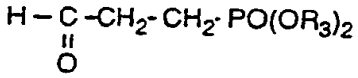
Claim 1, wherein n is 1 and Z represents $-CH_2PO(OR_3)_2$, which comprises:

reacting a (1,2,4)-triazole represented by formula (12):



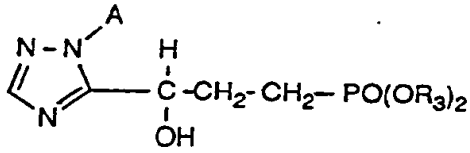
(12)

wherein A represents a group which is a protective group or is C_1-C_4-alkyl; with an aldehyde compound represented by the formula (23):



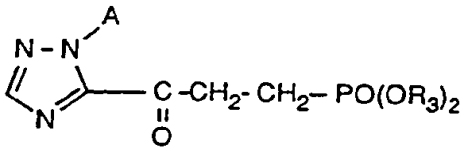
(23)

wherein R_3 has the same meaning as defined above, to form a 3-((1,2,4)-triazol-5-yl)-3-hydroxypropyl-phosphonate represented by formula (24):



(24)

wherein R_3 and A have the same meanings as defined above; converting the 3-((1,2,4)-triazol-5-yl)-3-hydroxypropyl-phosphonate to 3-(1H-1,2,4-triazol-5-yl)-3-hydroxy-propyl-phosphonic acid or phosphonate or oxidizing said 3-((1,2,4)triazol-5-yl)-3-hydroxypropyl-phosphonate to form a 3-((1,2,4)-triazol-5-yl)-3-oxopropyl-phosphonate represented by formula (25)



(25)

wherein R_3 and A have the same meanings as defined in Claim 1, followed by conversion into 3-(1H-1,2,4-triazol-5-yl)-3-oxopropyl-phosphonic acid or phosphonate.

14. A herbicidal composition comprising as the active ingredient at least one of the compounds represented by formula (2) as claimed in Claim 3.

15. A fungicidal composition comprising as the active ingredient at least one of the compounds represented by formula (2) as claimed in Claim 3.

16. A method of controlling undesired plant growth, which comprises applying an effective amount of an active substance of the formula (2) according to claim 3, or a composition comprising this active substance according to claim 14, to the plants or their environment.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP 92/00485

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07F9/6518; A01N57/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07F ; A01N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	EP,A,0 078 613 (IMPERIAL CHEMICAL INDUSTRIES PLC) 11 May 1983 cited in the application see the whole document	1-16
A	EP,A,0 065 216 (HOECHST AG) 24 November 1982 see the whole document	1-16
A	EP,A,0 275 821 (CIBA-GEIGY AG) 27 July 1988 see the whole document	1-13

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
15 JUNE 1992	09. 07. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	RINKEL L.J.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. JP 9200485 SA 58435

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/06/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0078613	11-05-83	AU-B- 550022	27-02-86
		AU-A- 8961182	12-05-83
		CA-A- 1179679	18-12-84
		GB-A- 2114133	17-08-83
		JP-A- 58088397	26-05-83
		US-A- 4439428	27-03-84
EP-A-0065216	24-11-82	DE-A- 3118257	02-12-82
		JP-A- 58023700	12-02-83
EP-A-0275821	27-07-88	AU-B- 607722	14-03-91
		AU-A- 8145387	26-05-88
		DE-A- 3776880	02-04-92
		JP-A- 63150291	22-06-88
		US-A- 4939130	03-07-90
		ZA-A- 8708698	23-05-88